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PATENT INFORMATION:	US 6562905	B1	20030513	
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APPLICATION INFO.:	US 2000-647846		20001109	(9)
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PRIORITY INFORMATION:	FI 1998-788	19980406
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DOCUMENT TYPE:	Utility	
FILE SEGMENT:	GRANTED	
PRIMARY EXAMINER:	Nutter, Nathan M.	
LEGAL REPRESENTATIVE:	Birch, Stewart, Kolasch & Birch, LLP	
NUMBER OF CLAIMS:	8	
EXEMPLARY CLAIM:	1	
NUMBER OF DRAWINGS:	2 Drawing Figure(s); 2 Drawing Page(s)	
LINE COUNT:	835	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB The present invention concerns a bimodal film-making HDPE composition, a process for the preparation thereof, a film prepared thereof and a film-making process. The composition comprises at least one polyethylene component having a relatively low molecular weight and another polyethylene component having a relatively high molecular weight. The composition has a shear thinning index defined by the relationship:

$$SHI.sub.5/300 \leq 0.00014 \eta.sub.5kPa + 78$$

wherein

$\eta.sub.5kPa$ is the complex viscosity at $G^*=5$ Pa and

$SHI.sub.5/300$ is the ratio of complex viscosity at $G^*=5$ kPa to the complex viscosity at $G^*=300$ kPa.

By means of the invention it is possible to produce material for making HDPE blown films with good mechanical properties in a process where the whole range of PE products from LLD to HD can be produced.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L4 ANSWER 2 OF 2 USPATFULL on STN

ACCESSION NUMBER: 96:75487 USPATFULL
 TITLE: Process for the production of polypropylene
 INVENTOR(S): Goode, Mark G.; Hurricane, WV, United States
 PATENT ASSIGNEE(S): Union Carbide Chemical & Plastics Technology Corporation, Danbury, CT, United States (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 5548042		19960820
APPLICATION INFO.:	US 1994-293473		19940819 (8)
DOCUMENT TYPE:	Utility		
FILE SEGMENT:	Granted		
PRIMARY EXAMINER:	Weber, Thomas R.		
LEGAL REPRESENTATIVE:	Bresch, Saul R.		
NUMBER OF CLAIMS:	8		
EXEMPLARY CLAIM:	1		
LINE COUNT:	1170		

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

AB A process comprising contacting propylene in two reaction zones connected in series, under gas phase polymerization conditions, with a transition metal catalyst system comprising

(a) introducing the catalyst into the first reaction zone;

(b) partially deactivating the catalyst and simultaneously increasing the monomer level to achieve a desired resin productivity in the first zone; and

(c) transferring resin together with catalyst from the first zone to the second zone having purged the deactivator or added activator in sufficient amount to achieve a desired resin productivity in the second zone.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

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L4 ANSWER 1 OF 2 USPATFULL on STN

DETD The shear thinning index, SHI.sub.5/300, is defined as the ratio of the viscosity at $G^*=300$ kPa to the complex viscosity at $G^*=5$ kPa. It is a measure of the molecular weight distribution. In the case of the bimodal polyethylene, the shear thinning index is most effectively **controlled** by the **split**, or the ratio of the fraction of the low molecular weight component to the fraction of the high molecular weight component in the final composition. Thus, to increase the shear thinning index one has to increase the fraction of the low molecular weight component. The shear thinning index is to some extent also influenced by the molecular weights of the low and high molecular weight components.

DETD To produce the polymer compositions, ethylene is polymerized in the presence of a suitable catalyst, preferably a Ziegler-Natta catalyst (cf. below) or a single-site catalyst, at an elevated temperature and pressure. Polymerization is carried out in a series of **polymerization reactors** selected from the group of slurry and gas phase reactors. A loop reactor is a particularly preferred embodiment of polymerization in slurry reactors. The relatively high molar mass portion and the relatively low molar mass portion of the product can be prepared in any order in the reactors.

DETD In addition to the actual **polymerization reactors** used for producing the bimodal ethylene homo- or copolymer, the polymerization reaction system can also include a number of additional reactors, such as prereactors. The prereactors include any reactor for pre-polymerizing the catalyst and for modifying the olefinic feed, if necessary. All reactors of the reactor system are preferably arranged in series (in a cascade).

DETD Thus, in the first step of the process, ethylene with the optional comonomer(s) together with the catalyst is fed into the first **polymerization reactor**. Along with these components hydrogen as a molar mass regulator is fed into the reactor in the amount required for achieving the desired molar mass of the polymer. Alternatively, the feed of the first reactor can consist of the reaction mixture from a previous reactor, if any, together with added fresh monomer, optional hydrogen and/or comonomer and cocatalyst. In the presence of the catalyst, ethylene and the optional comonomer will polymerize and form a product in particulate form, i.e. polymer particles, which are suspended in the fluid circulated in the reactor.

DETD The production split between the relatively high molar mass **polymerization reactor** and the relatively low molar mass **polymerization reactor** is 5-95:95-5. Preferably, 5 to 50%, in particular 10 to 50%, of the ethylene homopolymer or copolymer is produced at conditions to provide a polymer having a MFR.sub.2 of 100 g/10 min or more and constituting the low molar mass portion of the polymer, and 95 to 50%, in particular 90 to 50%, of the ethylene homopolymer or preferably copolymer is produced at such conditions that the final polymer has an MFR.sub.21 of less than 50 g/10 min, in particular about 3 to 50 g/10 min and constituting the high molar mass portion of the polymer. The density of the low molar mass portion is preferably over 960 kg/m.sup.3 and the density of the final polymer is preferably 940 to 965 kg/m.sup.3.

DETD The total process is, according to a preferred embodiment, conducted as

follows. The bimodal high density polyethylene film material is prepared in a process comprising a loop and a gas phase reactor in the presence of an active catalyst. The loop reactor is operated in super critical conditions, and thus the temperature and pressure of the reactor exceed the critical temperature and pressure of the fluid. Propane diluent, catalyst, ethylene and hydrogen are introduced into the reactor, so that an ethylene homopolymer having an MFR.sub.2 of about 300-1000 g/10 min is formed. The hydrocarbon slurry is withdrawn from the loop reactor, either continuously or intermittently, and the hydrocarbons are separated from the polymer. The polymer containing the active catalyst is then introduced into a gas phase reactor, where additional ethylene, comonomer, hydrogen and, optionally, an inert gas is introduced and the polymerisation is continued so as to provide a final composition with an MFR.sub.21 of about 4-12 g/10 min, a density of 940-965 kg/m.sup.3, **reactor split** of about (37-43)/(57-63). The polymer is then taken out of the gas phase reactor, either continuously or intermittently, the hydrocarbons are separated from the polymer and the polymer is compounded using a counterrotating twin screw extruder.

DETD According to another preferred embodiment of the invention, the total process is conducted as follows. The bimodal high density polyethylene film material is prepared in a process comprising a loop and a gas phase reactor in the presence of a catalyst prepared by depositing titanium tetrachloride on a magnesium dichloride carrier so that the catalyst contains no silica support. Alternatively, a catalyst prepared on silica carrier comprising magnesium dichloride, as disclosed in Example 1, can be used. The loop reactor is operated in super critical conditions, and thus the temperature and pressure of the reactor exceed the critical temperature and pressure of the fluid. Propane diluent, catalyst, ethylene and hydrogen are introduced into the reactor, so that an ethylene homopolymer having an MFR.sub.2 of about 300-1000 g/10 min is formed. The hydrocarbon slurry is withdrawn from the loop reactor, either continuously or intermittently, and the hydrocarbons are separated from the polymer. The polymer containing the active catalyst is then introduced into a gas phase reactor, where additional ethylene, comonomer, hydrogen and, optionally, an inert gas is introduced and the polymerisation is continued so as to provide a final composition with an MFR.sub.21 of about 4-12 g/10 min, a density of 940-965 kg/m.sup.3, **reactor split** of about (37-43)/(57-63). The polymer is then taken out of the gas phase reactor, either continuously or intermittently, the hydrocarbons are separated from the polymer and the polymer is compounded using a corotating or counterrotating twin screw extruder.

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L4 ANSWER 2 OF 2 USPATFULL on STN

SUMM The amount of resin (by weight) produced in each stage is usually given in terms of a weight ratio. This ratio is referred to as the split ratio. Thus, in a two stage process, the split ratio between the first and second stages can be 5:95 to 95:5, and in a three stage process, the split ratio between the first, second, and third stages can be 5:5:90 to 90:5:5 with many variations. The **split** can be **controlled** by the basic process of the invention, but, as an auxiliary control, the residence time in each stage can be adjusted by the addition of a dense non-reactive gas such as propane to the stage where the adjustment is desired, by the manipulation of the superficial gas velocity of the fluidizing gas, again in the stage where the adjustment is desired, or by changing the height of the fluid bed in the stage where the adjustment is desired.

SUMM Various deactivating compounds or "activity retarders" are mentioned in U.S. Pat. No. 5,066,736. They are also known as poisons or kill agents. Generally, the deactivating compounds which must be purged are those

such as carbon monoxide which do not react with the aluminum alkyls, the conventional reactivating compounds. Other deactivating compounds react mildly with the aluminum alkyls, such as carbon dioxide, nitrogen monoxide and sulfur dioxide, and can be purged from the resin and/or reactivated with activating compounds. Other deactivating compounds may react more strongly with the aluminum alkyl such as organic carbonyls including esters, ethers, alcohols, aldehydes, and ketones, and sulfides, water, oxygen, amines, and phthalate compounds. They may be purged to a degree from the resin, yet generally require the addition of an activator to restore the residual catalyst productivity. It should be noted that oxygen and water may be deleterious to the operation of the **polymerization reactor(s)** because of the possibility of "sheeting". Other deactivating compounds such as silicon containing carbonyl compounds, which have other uses in the **polymerization reactor**, can be used for the purpose of deactivation if the dual purpose can be accommodated.

SUMM To achieve the desired productivity in the first reactor, the monomer level is increased beyond the amount sufficient to counter the effect on productivity of the deactivation. This is necessary because the resulting decrease in the first reactor residence time passes increased levels of reactive catalyst to the second reactor. The resulting increase in catalyst productivity in the second reactor means that a greater fraction of the polymer is made there, and requires that the monomer levels in the first reactor be increased to maintain the desired **split between reactors**. The amount of deactivating agent and monomer level in the first reactor incrementally increases until a constraint is reached such as the maximum working pressure of the reactor vessel, excessive condensation of the cycle gas, or that the polymer fluidized bulk density approaches the minimum level required for stable fluidization, i.e., about six pounds per cubic foot. Operation at the highest allowable monomer pressure in the first reactor insures the optimum catalyst productivity and the minimum polymer average residence time for the overall process. The optimal amount of deactivating agent added to the reactor corresponds to operation at the highest monomer level in the first reactor. At these conditions, monomer levels in both reactors are at the highest allowable levels. Further increases in the amount of deactivating agent result in decreased production in the first reactor such that the overall productivity of the catalyst is sacrificed in order to produce the desired split of polymer in each reactor. For best performance, the monomer level in the second reactor should be near the maximum level.

SUMM It is possible to control the fraction of polymer made in each reactor by manipulating the purge or reactivation in the second reactor, or by controlling the partial pressure in the second reactor. It is also possible to **control the split** by manipulating the amount of deactivating agent added to the first reactor or by fixing the amount of deactivating agent and controlling the monomer level in the first reactor. A combination of these techniques can be used for process control, but the best catalyst productivity and minimum overall residence time is achieved when both reactors operate near their maximum allowable monomer levels and the residual productivity of the catalyst is fully recovered in the second reactor.

SUMM The advantages of this invention are improved catalyst productivity and reduced average residence time in linked gas phase fluidized bed **polymerization reactors**. This is accomplished by the addition of temporary deactivating agents to a first reactor causing an increase in the monomer level to maintain the desired catalyst productivity. This also increases the density of the fluidizing gas, and that decreases the fluidized bulk density of the particulate polymer. The result is a decrease in the average residence time of the polymer and catalyst particles in the first reactor. Therefore, because the

catalyst productivity decays exponentially with time, the average residual productivity of the catalyst passed to the subsequent reactor is increased. The catalyst productivity in the second reactor is recovered by purging or by the addition of an activating agent. The invention is easy to implement and control on a commercial scale. It improves the overall economics of the process and allows the production of a broader range of products in an existing polymerization facility.

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COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

35.70

35.91

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